

information has been included in the tunneling model.

In an earlier attempt<sup>8</sup> to systematize transfer excitation functions the measured cross sections were plotted vs  $E^*$ , where  $E^* = E_{c.m.} - E_{\text{barrier}} + Q$ . The quantity  $E^*$  is the kinetic energy available to the system at the time of contact after the transfer has occurred. Excitation functions plotted in this manner, with a few exceptions, tended to group together. These exceptions,  $\text{Mg}^{24}$ ,  $\text{Be}^9$ , and  $\text{C}^{12}$ , gave the curve a banded structure, that is, a main curve flanked by two satellites. It was hoped that with a few exceptions a "universal curve" existed for transfer reactions and that it could be used to predict unknown cross sections by the calculation of the quantity  $E^*$ . Fisher *et al.*,<sup>9</sup> at the suggestion of Breit, replotted transfer cross sections vs the expression  $[E_{c.m.} - E_{\text{barrier}} + Q/2]$ . Their "universal curve" brought some excitation functions closer together but displaced others. The over-all curve retained the three bands but the two satellites, now referring to reactions on different targets than in the first plot, were displaced to the same side of the main group.

In Fig. 4 the available single-nucleon transfer cross sections at low incident energies are plotted vs  $E^*$ . Dotted curves represent the five excitation functions obtained in this work, dashed curves show the data of

Perkin *et al.*,<sup>18</sup> while the solid curves represent the earlier data obtained with  $\text{N}^{14}$  beams. Not all excitation functions are shown in the diagram because some curves overlap and displaying these would tend to be confusing. A sufficient number of curves is shown, however, so that it is readily seen that in fact no "universal curve" exists. Reactions whose  $E^*$  values are about  $-7$  or  $-8$  MeV would have been expected from the earlier "universal curve" to have extremely small cross sections, but are seen to possess cross sections of a few millibarns. Also, instead of being closely grouped, the curves are spread over a wide range of  $E^*$ . A trend can be observed from Fig. 4, i.e., the higher the atomic number of the target the higher the cross section for a given value  $E^*$ . Plotting the cross sections in the manner of Fisher *et al.*,<sup>9</sup> does not bring about any additional clustering around a "universal curve."

#### ACKNOWLEDGMENTS

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## Melting and Polymorphism at High Pressures in Some Group IV Elements and III-V Compounds with the Diamond/Zinblende Structure\*

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The fusion curves of several elements and III-V compounds crystallizing in the diamond/zinblende structure have been determined to 50, or sometimes 70, kbar by means of differential thermal analysis. The melting slopes are (in  $^{\circ}\text{C}/\text{kbar}$ ): Si,  $-5.8$  (lower bound); Ge,  $-3.8$ ; InAs,  $-4.3$ ; GaAs,  $-3.4$ ; InP,  $-2.9$ ; AlSb,  $-6.9$  (provisional); GaSb,  $-5$ . Gallium antimonide has a triple point near 56.5 kbar and  $385^{\circ}\text{C}$ ; its high pressure metallic polymorph melts with an initial slope of  $+3.4$   $^{\circ}\text{C}/\text{kbar}$ . Progressively more negative slopes for the melting of the diamond/zinblende structures are apparently correlated with increasing atomic volume and decreasing normal melting point. Extension of these correlations suggests that diamond melts with only a slightly negative slope. The sequence of pressure-induced polymorphic transitions strikingly reflects straightforward increases in coordination.

### I. INTRODUCTION

THE diamond and the related zinblende type structure is a consequence of tetrahedrally coordinated atoms, with predominantly covalent binding. The Group IV elements, germanium and silicon as well as carbon and gray tin, crystallize in such a structure, as do many of the binary equiatomic compounds formed between Group III and V elements.

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The semiconducting properties of germanium and silicon especially, and also of the III-V compounds have received a great deal of attention. The band structures of many of these have been explored by a variety of techniques including, recently, the effects of pressure.<sup>1</sup> The study<sup>2</sup> of the electrical properties, for instance, of these semiconductors at moderately high pressures has contributed to the understanding of the conduction mechanisms in terms of pressure coefficients

<sup>1</sup> W. Paul, J. Appl. Phys. **32**, 2082 (1961).

<sup>2</sup> W. Paul, J. Phys. Chem. Solids **8**, 196 (1959); A. Sagar and R. C. Miller, J. Appl. Phys. **32**, 2073 (1961).

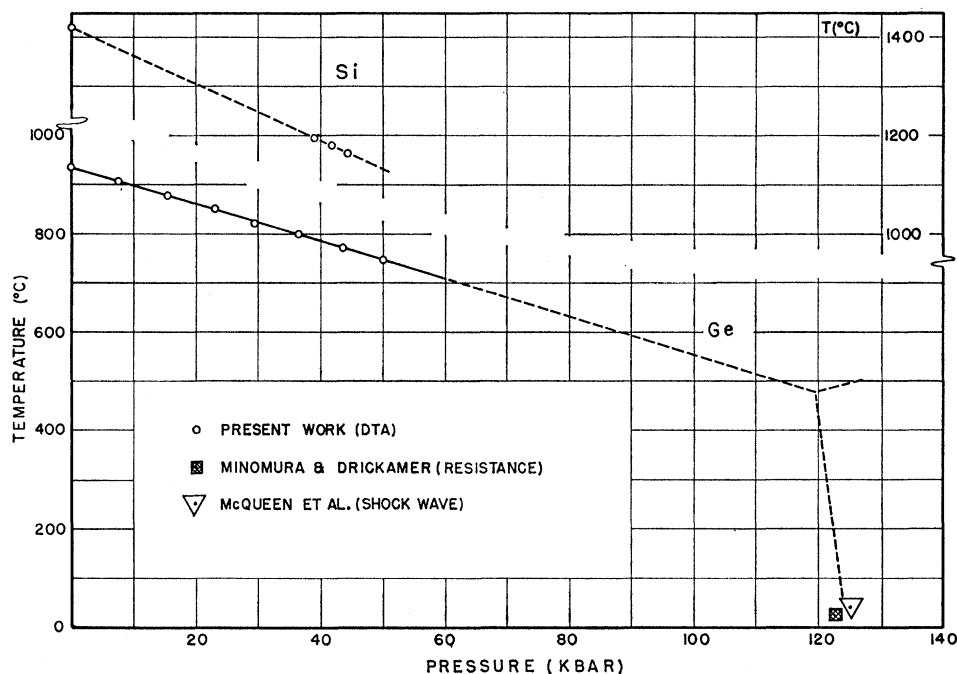


FIG. 1. Melting curves for silicon and germanium and proposed phase relations for germanium.

for the energy gaps between the valence band maxima and conduction band minima.

Gebbie *et al.*<sup>3</sup> initially studied indium antimonide up to 70 kbar and found a large discontinuous resistance drop near 30 kbar and room temperature, which was attributed to melting. Jayaraman, Newton, and Kennedy,<sup>4</sup> working with the technique of differential thermal analysis (DTA), found that the melting curve of InSb had a slope of  $-10^{\circ}\text{C}/\text{kbar}$  which broke off sharply at  $335^{\circ}\text{C}$  and 19.4 kbar, assuming a positive slope thereafter. A solid-solid transition at 22.5 kbar and room temperature was established, in which the semiconducting phase transformed to a metallic phase with a change of volume of  $\approx 20\%$ . The solid-solid boundary, as determined by the volume method, intersected the break in the melting curve and thus verified the triple point. Jayaraman *et al.*<sup>4</sup> drew an analogy between tin and isoelectronic InSb and suggested that the structure of InSb II was closely related to that of white tin.

In work up to 500 kbar, Minomura and Drickamer<sup>5</sup> have recently reported discontinuous drops in resistance for Ge, Si, and a number of III-V compounds. These semiconducting to metallic transitions are apparently very similar to that of InSb.

The need for determinations of the phase boundaries at high pressures for the several elements and compounds possessing the diamond/zincblende structure

<sup>3</sup> H. A. Gebbie, P. L. Smith, I. G. Austin, and J. H. King, *Nature* **188**, 1095 (1960).

<sup>4</sup> A. Jayaraman, R. C. Newton, and G. C. Kennedy, *Nature* **191**, 1288 (1961).

<sup>5</sup> S. Minomura and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 451 (1962).

seemed clear. This investigation was undertaken in order to obtain these data and then attempt to delineate the structural similarities among these materials, especially with respect to the occurrence and identification of the high pressure polymorphs.

## II. EXPERIMENTAL PROCEDURES

Pressures up to 50 kbar were generated in a piston-cylinder device previously described.<sup>6,7</sup> Higher pressures were obtained with a double-stage apparatus, also previously described.<sup>8</sup> Transitions were detected by means of differential thermal analysis.<sup>7</sup>

Friction corrections were made in the usual manner<sup>8</sup> and pressures are believed accurate to  $\pm 1.0$  kbar up to 50 kbar and  $\pm 2$  kbar at higher pressures. In the absence of reliable pressure corrections for chromel-alumel thermocouples, values from the standard tables were used. Temperatures were determined to  $\pm 3^{\circ}\text{C}$ , with the DTA signal obtained on heating taken for the melting point.

Polycrystalline semiconductor grade materials were used throughout. The problem of finding suitable containers for these several materials is discussed below, together with the other experimental details peculiar to each substance. After the high temperature high pressure runs, specimens were usually examined for contamination by means of x-ray diffraction.

<sup>6</sup> G. C. Kennedy and P. N. Lamori, *J. Geophys. Res.* **67**, 851 (1962).

<sup>7</sup> G. C. Kennedy and R. C. Newton, in *Solids Under Pressure*, edited by W. Paul and D. Warschauer (McGraw-Hill Book Company, Inc., New York, 1962).

<sup>8</sup> A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, *J. Phys. Chem. Solids* **24**, 7 (1963).

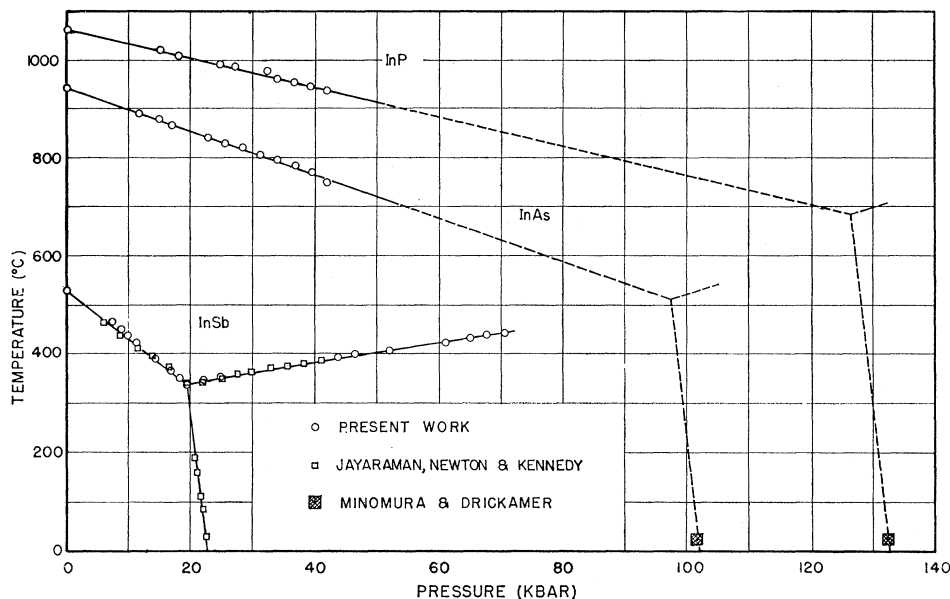


FIG. 2. Melting curves for indium phosphide, indium arsenide and indium antimonide. Also shown are the phase relations for InSb and the proposed boundaries for InAs and InP.

### III. EXPERIMENTAL RESULTS

#### Silicon

It was anticipated that the very reactive molten silicon would alloy rapidly with metallic containers and, thus, yield an apparent melting point below the true one. This was borne out in several experiments with molybdenum and tantalum. The highest melting points obtained from the best run are plotted in Fig. 1. The melting slope gotten by connecting these data with the normal melting point is found to be  $-5.8^{\circ}\text{C}/\text{kbar}$ , but this is best considered only as a lower bound; the calculated initial melting slope is about  $-4.2^{\circ}\text{C}/\text{kbar}$ . After the first couple of meltings of silicon, the DTA signal became somewhat smeared out, indicative of alloying. This was verified by the post-mortem x-ray diffraction examination.

A linear extrapolation of the present, tentative melting slope for the diamond/zincblende structure to about 200 kbar<sup>5</sup> at the expected triple point with the metallic, white-tin-like<sup>9</sup> phase suggests that the lowest temperature for the existence of liquid silicon is  $\sim 260^{\circ}\text{C}$ .

#### Germanium

The melting points obtained for germanium encapsulated in tantalum are plotted in Fig. 1. The present data extrapolate to the accepted normal melting point, in contrast to those of Hall,<sup>10,11</sup> who initially worked out the fusion curve. The slope of the melting curve is  $-3.8^{\circ}\text{C}/\text{kbar}$  compared to the calculated value of  $-2.9^{\circ}\text{C}/\text{kbar}$ .

<sup>9</sup> J. C. Jamieson, *Bull. Geol. Soc. Am.* 76A (1962); (unpublished data); *Science* 139, 762 (1963).

<sup>10</sup> H. T. Hall, *J. Phys. Chem.* 59, 1144 (1955).

<sup>11</sup> F. P. Bundy and H. M. Strong, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 13, p. 81.

The discontinuous change in resistance of germanium<sup>5</sup> at 120–125 kbar and  $25^{\circ}\text{C}$  is indicative of the semiconducting to metallic transition and this transformation has been verified by shock wave work.<sup>12</sup> Jamieson<sup>9</sup> has shown the structure of the metallic phase to be similar to that of white tin. The proposed phase boundaries are indicated in Fig. 1, assuming little curvature of the fusion curve.

#### Indium Antimonide

Jayaraman, Newton, and Kennedy<sup>4</sup> have previously determined the fusion curve of InSb to 50 kbar. Further experiments were performed to 65 kbar with InSb contained in tantalum but no new phase, akin perhaps to Sn II, was detected. All data are plotted in Fig. 2. No other transformations could be detected with DTA during a careful search of the high temperature stability field of the diamond/zincblende structure.

#### Indium Arsenide and Indium Phosphide

Sharp melting signals were detected for InAs and InP encapsulated in molybdenum. The melting slopes are determined as  $-4.3^{\circ}\text{C}/\text{kbar}$  for InAs and  $-2.9^{\circ}\text{C}/\text{kbar}$  for InP. The resistance measurements of Minomura and Drickamer<sup>5</sup> indicate semiconducting to metallic transitions at  $25^{\circ}\text{C}$  and 100–103 kbar for InAs and 130–135 kbar for InP. The proposed phase relations for InAs and InP are given in Fig. 2, together with the present results. It is interesting to note that a plot of  $dT/dP$  vs normal melting temperature for the indium compounds, InP, InAs and InSb, yields a linear relation (Fig. 3).

<sup>12</sup> R. G. McQueen, S. P. Marsh, and J. Wackerle, *Bull. Am. Phys. Soc.* 7, 447 (1962).

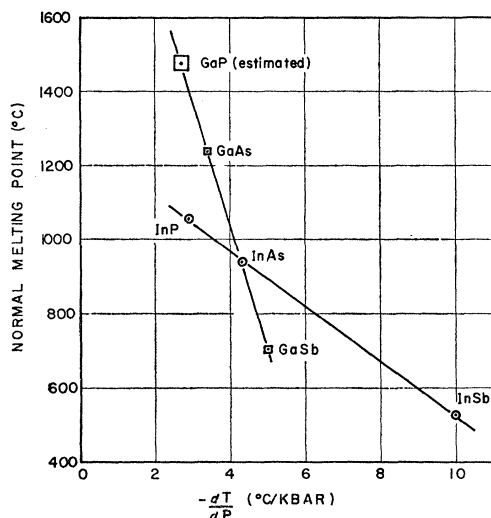


FIG. 3. Plot of melting slope of diamond/zincblende structure vs normal melting point for the gallium and indium compounds, respectively. The melting slope of GaP is estimated by linear extrapolation.

#### Gallium Antimonide

Titanium proved to be a satisfactory material for containing GaSb. The triple point between the liquid and two solid phases was located near 56.5 kbar and 385°C, as shown in Fig. 4. The resistance drop found by Minomura and Drickamer<sup>5</sup> at 70–85 kbar and 25°C, which is presumably indicative of the semiconducting to metallic transition, is believed to lie too high in pressure, perhaps owing to the sluggishness of the transition. The suggested solid-solid phase boundary is plotted in Fig. 4. For GaSb, the initial melting slope for the diamond/zincblende structure is  $-5.0^\circ\text{C}/\text{kbar}$  with some curvature prior to the triple point with the metallic phase. The latter melts with an initial slope of  $3.4^\circ\text{C}/\text{kbar}$ . The entropy of fusion for GaSb is estimated as  $\sim 5.8$  eu from the volume change of fusion of  $-7.0\%$ <sup>13</sup> and the present value for  $dT/dP$ .

#### Gallium Arsenide

Tantalum was used to contain GaAs and proved to be excellent, which was not surprising since previous work on the melting of gallium<sup>8</sup> and arsenic<sup>14</sup> had been successfully carried out in tantalum. The DTA signals were well defined and the points on the fusion curve (Fig. 4) accurately determined. The initial melting slope is  $-3.4^\circ\text{C}/\text{kbar}$ .

In work involving arsenic, it is imperative to have the container well stoppered to prevent its escape. For example, in the case of Group III–arsenic compounds, deviation from stoichiometry would only result in a smearing of the signal for melting as detected by

<sup>13</sup> H. P. Mokrskii and A. R. Regel, *J. Tech. Phys.* **22**, 1282 (1952).

<sup>14</sup> A. Jayaraman, W. Klement, and G. C. Kennedy (unpublished data).

DTA but would result in anomalously low resistances, because of the slight excess of metal.

If the linear relation found for the indium compounds when  $dT/dP$  is plotted against normal melting temperature also holds for the gallium compounds, the initial melting slope for GaP may be estimated as  $\sim -2.7^\circ\text{C}/\text{kbar}$  (Fig. 3).

#### Aluminum Antimonide

The melting of AlSb was studied with the compound encapsulated in molybdenum. Signals were obtained at pressures up to 40 kbar, and suggested that the melting slope was  $-6.9^\circ\text{C}/\text{kbar}$ . Unfortunately, the extrapolation to zero pressure yielded a normal melting point of  $\sim 1032^\circ\text{C}$  which falls far below the well-documented<sup>15</sup> melting point at  $1060^\circ\text{C}$ . It is probable that the specimens picked up some moisture during preparations for the run.

#### Collected Thermodynamic Data

The data for the Group IV elements and III–V compounds which are pertinent to the following discussions are collected in Table I.

#### IV. DISCUSSION

The suggestion of Jayaraman, Newton, and Kennedy<sup>4</sup> that the zincblende InSb II transformation is analogous to the gray-white Sn transition merits further consideration inasmuch as this may be a general feature

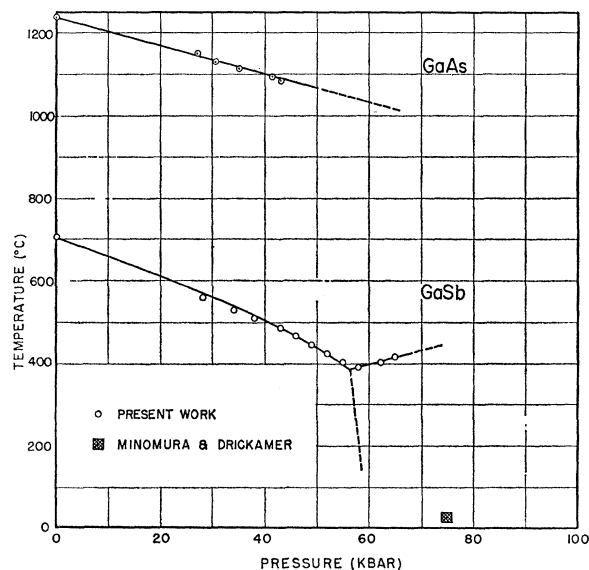


FIG. 4. Melting curves for gallium arsenide and gallium phosphide. The proposed GaSb solid-solid boundary does not connect with the resistance discontinuity found by Minomura and Drickamer (reference 5) which is believed to be due to an "overshooting" of the transition.

<sup>15</sup> M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

TABLE I. Thermodynamic and other data for some polymorphs of Group IV elements and some III-V compounds.

Element or compound	Atomic volume ( $\text{\AA}^3/\text{atom}$ ) <sup>a,b</sup> at room temperature	Energy gap (eV)	Diamond/zincblende polymorph (zero pressure)					Coordinates of triple point between liquid, diamond/zincblende and metallic polymorph		Metallic polymorph melting slope ( $^{\circ}\text{C}/\text{kbar}$ )
			Normal melting point ( $^{\circ}\text{C}$ )	Entropy of fusion (eu)	Volume change-fusion (%)	Melting slope ( $^{\circ}\text{C}/\text{kbar}$ ) calc expt				
C	5.7	5.3 <sup>c</sup>	...	...	...	...	...	...	...	
Si	20.1	1.21 <sup>c</sup>	1420 <sup>a</sup>	6.5 <sup>f</sup>	-9.6 <sup>f</sup>	-4.2	-5.8 <sup>i</sup>	...	...	
Ge	21.5	0.803	936 <sup>a</sup>	6.0 <sup>f</sup>	-5.5 $\pm$ 0.5 <sup>e</sup>	-2.9	-3.8	~115 kbar, ~500 $^{\circ}\text{C}$ (est.)	...	
Sn	34.2	0.08 <sup>e</sup>	...	(5.07-calc)	(~21-calc)	(-18.3)	...	-4 kbar, 220 $^{\circ}\text{C}$ (calc)	2.9	
InSb	34.0	0.2357 <sup>e</sup>	530 $\pm$ 3 <sup>e</sup>	7.43 $\pm$ 0.25 <sup>e</sup>	-13.7 $\pm$ 0.5 <sup>e</sup>	-9.1	-10	19.4 kbar, 335 $^{\circ}\text{C}$	2.3	
GaSb	28.5	0.813 <sup>d</sup>	706 <sup>a</sup>	~5.8 (calc)	-7.0 <sup>b</sup>	...	-5	56.5 kbar, 385 $^{\circ}\text{C}$	3.4	
AlSb	28.8	1.6 <sup>c</sup>	1060 <sup>a</sup>	...	...	...	-6.9 <sup>i</sup>	...	...	
InAs	27.8	0.360 <sup>d</sup>	942 <sup>a</sup>	...	...	...	-4.3	~100 kbar, ~500 $^{\circ}\text{C}$ (est.)	...	
GaAs	22.5	1.41 <sup>d</sup>	1238 <sup>a</sup>	...	...	...	-3.4	...	...	
AlAs	22.3	2.16 <sup>c</sup>	>1600 <sup>a</sup>	...	...	...	...	...	...	
InP	25.3	1.29 <sup>d</sup>	1060 <sup>a</sup>	...	...	...	-2.9	~125 kbar, ~700 $^{\circ}\text{C}$ (est.)	...	
GaP	20.2	2.2 <sup>c</sup>	1450-1500 <sup>a</sup>	...	...	~-2.7 (est.)	...	...	...	
AlP	20.2	3.1 <sup>c</sup>	...	...	...	...	...	...	...	

<sup>a</sup> See reference 15.

<sup>b</sup> See reference 18.

<sup>c</sup> See reference 1.

<sup>d</sup> H. Ehrenreich, *J. Appl. Phys.* **32**, 2155 (1961).

<sup>e</sup> See reference 17.

<sup>f</sup> A. Schneider and G. Heymer, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds* (Her Majesty's Stationery Office, London, 1959).

<sup>g</sup> N. H. Nachtrieb and N. Clement, *J. Phys. Chem.* **62**, 747 (1958).

<sup>h</sup> See reference 13.

<sup>i</sup> Provisional.

for all diamond/zincblende structures under pressure. Jamieson's recent identification<sup>9</sup> of the high pressure polymorphs of Ge, Si, and InSb as having the white tin structure strikingly verifies this proposal and gives additional impetus for a detailed examination of the structural characteristics of tin.

### Tin

The data of Kennedy and Newton<sup>7</sup> for the melting of white tin and Sn II and for the white tin-Sn II transition are plotted in Fig. 5. The *calculated* phase boundaries for the white tin-gray tin transformation, for the melting of gray tin and the probable connection between the Newton-Kennedy data and the resistance discontinuity found by Stager, Balchan, and Drickamer<sup>16</sup> are also plotted in Fig. 5.

The initial slope of the white tin fusion curve is calculated to be about 2.9 $^{\circ}\text{C}/\text{kbar}$ . Some curvature is manifested prior to the appearance of Sn II near 33 kbar and 305 $^{\circ}\text{C}$ .<sup>7</sup> The Sn II melting curve probably also exhibits some curvature, with the slope decreasing from the value at the triple point, viz., 5.0 $^{\circ}\text{C}/\text{kbar}$ .

<sup>16</sup> R. A. Stager, A. S. Balchan, and H. G. Drickamer, *J. Chem. Phys.* **37**, 1154 (1962).

The course of the white tin-gray tin transformation may be estimated via the Clausius-Clapeyron equation; at 13 $\pm$ 3 $^{\circ}\text{C}$ ,<sup>17</sup> the entropy of transition is 1.76 $\pm$ 0.08 eu<sup>17</sup> and the volume change, -4.29 cm<sup>3</sup>/mole<sup>18,19</sup> and thus  $dT/dP$  is about -58 $^{\circ}\text{C}/\text{kbar}$ . If the zero-pressure fusion data for white tin ( $\Delta S=3.31$  eu,<sup>17</sup>  $\Delta V=0.40$  cm<sup>3</sup>/mole<sup>19</sup>) are directly combined with the gray-white tin data, the triple point is computed to be near -4 kbar and 220 $^{\circ}\text{C}$  with a melting slope for gray tin of -18.3 $^{\circ}\text{C}/\text{kbar}$  (cf. Table I).

White tin, at zero pressure and room temperature, has a body-centered tetragonal structure, with 4 atoms/unit cell and an axial ratio of 0.545.<sup>18</sup> The elastic moduli<sup>20</sup> suggest that the axial ratio does not change appreciably with pressure; high-temperature x-ray diffraction and dilatometry work<sup>18</sup> indicates that the axial ratio increases only slightly with temperature. It is thus suggested that the coordination for a given

<sup>17</sup> R. Hultgren *et al.* (unpublished).

<sup>18</sup> W. B. Pearson, *Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pergamon Press, New York, 1958).

<sup>19</sup> A. D. Kirshenbaum and J. A. Cahill, *Trans. Am. Soc. Metals* **55**, 844 (1962).

<sup>20</sup> H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 214.

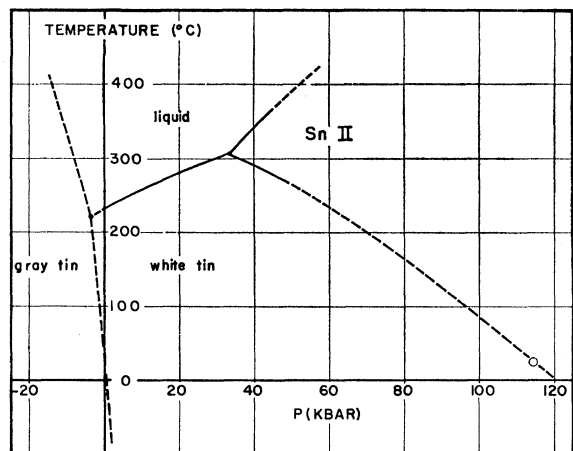


FIG. 5. Phase diagram of tin. Data for melting are from Kennedy and Newton (reference 7); their white tin-Sn II boundary is continued to the resistance discontinuity found by Stager *et al.* (reference 16). The gray tin phase boundaries are from calculation.

atom in the white tin structure does not vary appreciably over a range of pressure and temperature.

Although some workers choose to regard the gray-white tin transformation<sup>21</sup> as diffusionless, its sluggishness is well known. The white tin to Sn II transition,<sup>16</sup> however, is abrupt, without appreciable hysteresis and characterized by a very slight increase in resistance and, thus, may be somewhat more difficult to detect if and when an analogous transition occurs in the other materials. Jamieson<sup>9</sup> has recently identified Sn II as body-centered cubic and suggested a volume change of about 5% at the 113–115 kbar and 25°C transition point.

#### Analogies with the Behavior of Tin

The sequence of polymorphic transformations for tin, viz., diamond → white tin → body-centered cubic, with increasing pressure may be indicative of those to be found in the related substances investigated here. Since InSb is isoelectronic with tin and very similar in its several properties with gray tin, it might be expected that the transition to a body-centered cubic structure would occur at lower pressures than for the other diamond/zincblende materials.

Certain important features that might be expected of diamond/zincblende structures under pressure emerge from the phase diagrams of tin and indium antimonide. The fusion curve for the diamond/zincblende structure would have a negative melting slope until the transition to a metallic phase takes place. The volume change accompanying such a transition is large ( $\approx 20\%$ ) and  $dT/dP$  for the phase boundary is steeply negative.

The sluggishness of the gray-white tin and the InSb I–InSb II transitions at lower temperatures

suggest that, in the higher melting elements and compounds, the sluggishness would be still more pronounced. The “overshooting” of the semiconductor to metallic transition reported<sup>5,22</sup> for several compounds can thus be understood. The pressure value most nearly corresponding to equilibrium should be the lowest, which is also most readily obtainable with polycrystalline samples and at the higher temperatures.

If, for gallium antimonide, the triple point presently determined by melting is joined to the point determined from resistance change by Minomura and Drickamer<sup>5</sup> at room temperature, the slope is not as steep as seems to be characteristic of the diamond/zincblende-white tin transition. It is believed that there has been overshooting of the transition by Minomura and Drickamer<sup>5</sup> and the boundary should have a much steeper slope, as has been indicated in Fig. 5.

For GaAs, which is isoelectronic with Ge, two abrupt decreases in resistance were found<sup>5</sup>—one at 240–250 kbar and the other at 270–280 kbar, at room temperature. Minomura and Drickamer<sup>5</sup> attributed the former to melting and the latter to freezing. (The first transition seems to be prone to overshooting which must be considered quite uncharacteristic of melting.) However, this seems to be impossible, for the melting curve, as determined in the present investigation, has a slope of only  $-3.4^\circ\text{C}/\text{kbar}$  and at 240–250 kbar would not have come down anywhere near room temperature. The transitions are, in all probability, solid-solid ones.

#### Progressive Variation in Properties

As one moves down the periodic table, the Group IV elements and III–V compounds exhibit remarkably monotonic decreases in the normal melting points and energy gaps and also a steady increase in the molar volumes. There are also probably trends of decreasing Debye temperature and hardness and of increasing compressibility, although fewer measurements of these properties are available. This systematic variation may be said to reflect the strength of bonding. Although the bonding is purely covalent in the elements, ionic contributions are present in the III–V compounds as seen in the difference in the cleavage properties, for instance. The ionic character of the bonding is thought to increase in the sequence<sup>23</sup>

GaSb, InSb, GaAs, AlSb, InAs,

GaP, InP, AlAs, AlP, . . .

Despite the strikingly systematic variations in the several properties including energy gaps, detailed considerations of the band structures have shown that the conduction mechanisms are not the same for all of

<sup>22</sup> S. Minomura, G. A. Samara, and H. G. Drickamer, *J. Appl. Phys.* **33**, 3196 (1962).

<sup>23</sup> C. Hilsum and A. C. Rose-Innes, *Semiconducting III–V Compounds* (Pergamon Press, New York, 1961), p. 21.

<sup>21</sup> G. A. Busch and R. Kern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 1.

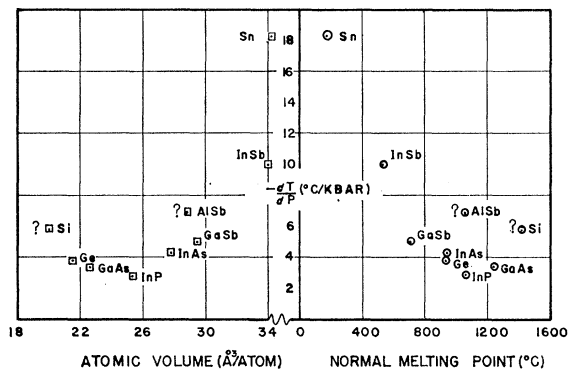


FIG. 6. Melting slopes for diamond/zincblende structures plotted against room temperature volume/atom and normal melting point, respectively. Increasingly negative melting slopes are roughly correlated with increasing atomic volume and with decreasing normal melting point.

the diamond/zincblende semiconductors. Specifically, the conduction band minima for silicon are located on the  $[100]$  axes<sup>24</sup> while the minima for germanium are on the  $[111]$  axes<sup>24</sup>; the pressure coefficients for these minima appear to be of different sign<sup>24,25</sup>: For the indium compounds, resistance increases with pressure whereas there are usually decreases, although not necessarily monotonic, for the other semiconductors prior to the phase changes. This may infer differences in the conduction mechanisms, such as the positions of the minima. It would thus appear that considerable caution has to be exercised when seeking correlations between the energy gap and the pressure and volume change of the transition to the metallic phase.

#### Correlations among the Fusion Data

The newly determined slopes of the fusion curves may be systematically correlated. A plot of  $-dT/dP$  vs atomic volume/atom in the diamond/zincblende structure shows a progressively more negative slope with increasing atomic volume (Fig. 6). There seems to be distinct deviations (i.e., less negative slopes) for the III-V compounds with increasing ionic character. As readily seen from Table I, the slopes of the fusion curves for the isoelectronic III-V compounds are somewhat less negative than the slopes for the corresponding Group IV elements. This may be directly related to the ionic contribution to the bonding present in the compound.

By plotting slope vs normal melting point, the slopes are found to be progressively less negative with increasing melting point (Fig. 6). Although these correlations are empirical and of uncertain meaning in the absence of a detailed theory, they may be useful in estimating melting relations for the other diamond/

zincblende structures not yet investigated experimentally.

#### The Phase Diagram of Carbon

A phase diagram for carbon was proposed by Jayaraman, Newton, and Kennedy<sup>26</sup> which featured a small negative slope for the melting of diamond and a more steeply melting slope for graphite with the graphite-diamond-liquid carbon triple point near 150 kbar and 3300°K and the diamond-carbon III-liquid triple point near 600 kbar and 2900°K. A positive slope for the melting of carbon III was indicated. The phase transformation reported by Alder and Christian<sup>27</sup> near 600 kbar was taken as indicative of a solid-solid transition.

Bundy<sup>28</sup> has recently presented some measurements for the melting of graphite at high pressures. A phase diagram for carbon was then proposed,<sup>29</sup> which includes the liquid-graphite-diamond triple point near 130 kbar and 4100°K, a steeply negative slope for the melting of diamond (including the shock wave results of Alder and Christian<sup>27</sup> for melting at 0.6 Mbar and 1300°K) and a liquid-diamond-carbon III triple point at a higher pressure and lower temperature than the Alder-Christian<sup>27</sup> datum. This proposal may be examined in light of the correlations herein proposed for the melting of diamond/zincblende structures.

First, the very small atomic volume and very high normal melting point of diamond suggest that the slope of the diamond fusion curve is *not* particularly steeply negative and may be less than  $-3^{\circ}\text{C}/\text{kbar}$ . Second, it is by no means established that the 15% volume change detected by Alder and Christian<sup>27</sup> necessarily corresponds to melting. Such volume changes are comparable in magnitude to those for the diamond/zincblende to white tin transitions in Sn,<sup>9</sup> InSb,<sup>4</sup> Ge,<sup>9</sup> Si,<sup>9</sup> etc. Also, the scatter in points on the Alder-Christian Hugoniot above 0.6 Mbar may be physically meaningful and related to the sluggishness of this sort of semiconductor to metallic transition and not necessarily attributable to experimental difficulties.<sup>27</sup>

Thus, the present point of view coincides with the previous proposal<sup>26</sup> that the shock wave datum<sup>27</sup> corresponds to a solid-solid transition and not to melting of diamond, that the phase boundary between diamond and carbon III is steep and that the diamond-liquid-carbon III triple point is near 0.6 Mbar and between 1300 and 4200°K, perhaps near 2700°K, if a slope of  $-3^{\circ}\text{C}/\text{kbar}$  is used. This would then be the lowest temperature at which liquid carbon exists, since the metallic polymorph would be expected to have a positive melting slope.

<sup>26</sup> A. Jayaraman, R. C. Newton, and G. C. Kennedy, International Conference on Industrial Diamonds, Paris, 1962 (unpublished).

<sup>27</sup> B. J. Alder and R. H. Christian, Phys. Rev. Letters **7**, 367 (1961).

<sup>28</sup> F. P. Bundy, Science **137**, 1055 (1962).

<sup>29</sup> F. P. Bundy, Science **137**, 1057 (1962).

<sup>24</sup> D. Long, J. Appl. Phys. **33**, 1682 (1962).

<sup>25</sup> R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 149.

### Increase in Coordination

The more efficient packing of atoms, resulting from increases in coordination, can be clearly seen in the sequence of polymorphic transitions. There are three nearest neighbors for the hexagonal graphite structure of carbon and isoelectronic BN, with the next highest coordination found in the hexagonal wurtzite structure. By transformation to the diamond/zincblende structure, the coordination is increased to precisely four. For the white tin structure, there are four nearest neighbors and two next nearest, more or less depending on the axial ratio. Exact sixfold coordination is realized in the NaCl structure.<sup>30</sup> In a similar way, eightfold coordination may be expected in the form of the CsCl structure (ordered) or as body-centered cubic (disordered). Further compression may then result in transitions to the random, close-packed structures.

Tin, which has been discussed at length previously in this paper, demonstrates much of this sequence. With increasing pressure, the diamond, then white tin, and then body-centered cubic structures appear. Upon further compression, it is anticipated that close-packed phases will be stable, perhaps in the sequence—face-centered cubic, then hexagonal close-packed—as is thought to occur for lead.<sup>31</sup>

The occurrence of a given structure obviously depends upon the relative free energies of the various phases and the absence of a given structure does not

<sup>30</sup> The disordered analog—a simple cubic structure with one atom/unit cell—does not seem to appear in the sequence. Also apparently absent is a structure similar to the simple hexagonal ( $c/a \sim 0.93$ ) phase found in the tin-rich binary alloys (see references 15 and 18) with cadmium, indium, and mercury, where the coordination is two plus three.

<sup>31</sup> W. Klement, J. Chem. Phys. **38**, 298 (1963).

detract from the *direction* of the packing sequence outlined above. Some structures appear to manifest higher entropies and, thus, exhibit a broader range of stability at the higher temperatures. This observation particularly refers to the graphite and body-centered cubic structures; the diamond/zincblende-white tin and face-centered cubic-hexagonal close-packed phase boundaries are expected to be quite steep.

The possibility of ordering in the multicomponent high pressure phases is also to be considered. For instance, InSb II may well be ordered—with possibly indium atoms at  $(0,0,0)$ ,  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and antimony atoms at  $(0, \frac{1}{2}, \frac{3}{4})$ ,  $(\frac{1}{2}, 0, \frac{1}{4})$ . To verify this by means of x-ray diffraction would be a difficult task because of the similarity in scattering powers. Ordering will be favored for those binary compounds where there is an appreciable difference in electronegativity between the constituent atoms. This factor will receive further discussion in a forthcoming paper on the high pressure polymorphs in some II-VI and I-VII compounds.

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